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### (54) CELLULOSE ESTER FILM AND ITS MANUFACTURING METHOD AND PROTECTIVE FILM FOR POLARIZING PLATE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a manufacturing method of cellulose ester films having a reduced retardation value (Rt value) in the thickness direction by preparing a cellulose ester dope without using a chlorine-based solvent.

SOLUTION: The cellulose ester films comprise at least one member of aliphatic dibasic acid diesters, trimellitic tri-esters, and phosphoric triesters. The manufacturing method and protective films for a polarizing plate are provided.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of a cellulose ester film useful to a polarizing plate protective film, and a cellulose ester film.

[0002]

[Description of the Prior Art] Now, the cellulose triacetate film is preferably used for the silver halide photosensitive material or the liquid crystal image display device from the characteristic without the transparency and optical defect.

The demand quality is developed every year.

[0003] On the other hand, restriction tends to be environmentally added to the use, and a chlorine-based hydrocarbon solvent like the methylene chloride which is a good solvent to the cellulose ester which makes cellulose triacetate representation has the request to the manufacturing method which does not use methylene chloride in recent years. However, it is difficult SUBJECT to replace the solvent of cellulose ester with a non-chlorine organic solvent, and to obtain the dope of good quality.

[0004] The following proposals are made to the above demands. For example, in JP,H9-95544,A and a 9-95557 gazette, the cooling solution process which used the organic solvent which consists of acetone substantially, or uses methyl acetate, acetone, and other non-chlorine organic solvents is proposed. To JP,H9-95538,A, ether other than acetone, In the method and JP,H11-21379,A which carry out the cooling dissolution using the organic solvent chosen from ketone or ester, cellulose triacetate is mixed with acetone and the method of applying the pressure of 0.98 - 490MPa is proposed.

[0005] However, it turned out that the film obtained using such a method has a problem that the thickness direction retardation value of a film becomes high.

[0006] The retardation value ( $R_{th}$  value) of a thickness direction is expressed with a following formula.

$R_{th} \text{ value} = (n_x + n_y) / (2 - n_z) \times d$  (the refractive index of the film of a direction (cross direction) in which refractive index of the film of the flow casting direction of a film and  $n_y$  of  $n_x$  are vertical to the flow casting direction, and  $n_z$  express the refractive index of the film of a thickness direction, and  $d$  expresses the thickness (nm) of a film, respectively.)

A problem that contrast when the  $R_{th}$  value became high and it sees from an oblique direction in the liquid crystal display of various systems, such as STN, TFT, and TN, falls and an angle of visibility becomes narrow arises.

[0007] In JP,H11-92574,A, 11-124445, and 11-246704, Although the method of mixing the lower fatty acid ester and the specific compound of cellulose with the organic solvent as for which more than 50 mass % contains acetone or methyl acetate, preparing a solution with a cooling solution process, and reducing the  $R_{th}$  value of a film by carrying out flow casting film production is proposed, it cannot be said that it is still enough.

[0008]

[Problem to be solved by the invention] The purpose of this invention prepares a cellulose ester dope, without using a chlorine-based solvent, and there is in providing the manufacturing method which obtains the cellulose ester film in which the retardation value ( $R_{th}$  value) of the thickness direction was reduced.

[0009]

[Means for solving problem] The purpose of describing this invention above was attained by the following composition.

[0010] (1) A cellulose ester film containing at least one sort of compounds expressed with a following general formula (1).

[0011]

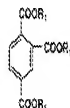
General formula (1) R expresses the alkyl group of the carbon numbers 1-10 among a R-OOC ( $\text{CH}_2$ )<sub>n</sub> COO-R type, and n expresses the integer of 4-10.

[0012] (2) A cellulose ester film containing at least one sort of compounds expressed with a following general formula (2).

[0013]

[Chemical formula 3]

一般式(2)



[0014]R<sub>1</sub> expresses the alkyl group of the carbon numbers 1-8 among a formula.

(3) A cellulose ester film containing at least one sort of compounds expressed with a following general formula (3).

[0015]

[Chemical formula 4]

一般式(3)



[0016]R<sub>2</sub> expresses the alkyl group of the carbon numbers 1-4 among a formula.

(4) The cellulose ester film of 1-3 given [said] in any 1 clause, wherein cellulose ester is lower fatty acid ester of cellulose.

[0017](5) The cellulose ester film of 1-4 given [said] in any 1 clause, wherein cellulose ester has a number average molecular weight of 70,000-300,000.

[0018](6) To the organic solvent which does not contain a chlorine-based solvent substantially, at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (1) above the boiling point in the ordinary pressure of the organic solvent, And a manufacturing method of the cellulose ester film exfoliating and drying the half-dry film which cast the dope produced by dissolving under the pressure conditions on which it does not foam on the base material, and was cast into the base material.

[0019](7) To the organic solvent which does not contain a chlorine-based solvent substantially, at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (2) above the boiling point in the ordinary pressure of the organic solvent, And a manufacturing method of the cellulose ester film exfoliating and drying the half-dry film which cast the dope produced by dissolving under the pressure conditions on which it does not foam on the base material, and was cast into the base material.

[0020](8) To the organic solvent which does not contain a chlorine-based solvent substantially, at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (3) above the boiling point in the ordinary pressure of the organic solvent, And a manufacturing method of the cellulose ester film exfoliating and drying the half-dry film which cast the dope produced by dissolving under the pressure conditions on which it does not foam on the base material, and was cast into the base material.

[0021](9) After cooling at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (1), and the organic solvent which does not contain a

chlorine-based solvent substantially at -100 °~-10 °, A manufacturing method of the cellulose ester film exfoliating and drying the half-dry film which cast the dope which might be warmed by 0 °~-120 ° in the cooling thing on the base material, and was cast into the base material.

[0022](10) The solution which might be pressurized by 50 atmospheres or more 2,000 atmospheres or less in the mixture of at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (1) and the organic solvent which does not contain a chlorine-based solvent substantially is cast on a base material, A manufacturing method of the cellulose ester film exfoliating and drying the half-dry film cast into the base material.

[0023](11) After cooling at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (2), and the organic solvent which does not contain a chlorine-based solvent substantially at -100 °~-10 °, A manufacturing method of the cellulose ester film exfoliating and drying the half-dry film which cast the dope which might be warmed by 0 °~-120 ° in the cooling thing on the base material, and was cast into the base material.

[0024](12) The solution which might be pressurized by 50 atmospheres or more 2,000 atmospheres or less in the mixture of at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (2) and the organic solvent which does not contain a chlorine-based solvent substantially is cast on a base material, A manufacturing method of the cellulose ester film exfoliating and drying the half-dry film cast into the base material.

[0025](13) After cooling at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (3), and the organic solvent which does not contain a chlorine-based solvent substantially at -100 °~-10 °, A manufacturing method of the cellulose ester film exfoliating and drying the half-dry film which cast the dope which might be warmed by 0 °~-120 ° in the cooling thing on the base material, and was cast into the base material.

[0026](14) The solution which might be pressurized by 50 atmospheres or more 2,000 atmospheres or less in the mixture of at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (3) and the organic solvent which does not contain a chlorine-based solvent substantially is cast on a base material, A manufacturing method of the cellulose ester film exfoliating and drying the half-dry film cast into the base material.

[0027](15) A manufacturing method of the cellulose ester film of 6-14 given [said] in any 1 clause, wherein an organic solvent contains methyl acetate not less than 50%.

[0028](16) A manufacturing method of the cellulose ester film of 6-15 given [said] in any 1 clause, wherein cellulose ester is lower fatty acid ester of cellulose.

[0029](17) A manufacturing method of the cellulose ester film of 6-16 given [said] in any 1 clause, wherein cellulose ester has a number average molecular weight of 70,000-300,000.

[0030](18) The polarizing plate protective film using the cellulose ester film of 1-5 given in any 1 clause.

[0031]This invention is explained in more detail below. The cellulose ester which constitutes the cellulose ester film of this invention, it is cellulose ester which has an acyl group of the carbon numbers 2-3 as a substituent, for example, cellulose triacetate, cellulose diacetate, cellulose acetate propionate, cellulose propionate, etc. are mentioned. The acyl group whose carbon number is four or more like cellulose acetate butyrate and cellulose-acetate-propionate butyrate may be contained. What consists only of an acyl group of the carbon numbers 2-3 is preferred, and especially cellulose triacetate and cellulose acetate propionate are especially preferred. As for the degree of substitution of an acyl group, it is preferred that it is 2.6-3.0. A film with good elevated temperature and tolerance which receives highly humid is obtained by making the degree of substitution into this range. As for the degree of substitution of an acetyl group, since the breaking strength of a film may become low too much if the degree of substitution of an acetyl group is too small not much, it is preferred that it is 1.4 or more.

[0032]The measuring method of the degree of substitution of an acyl group can be measured by ASTM-D 817-96.

[0033]The synthesizing method of the cellulose ester of this invention is compoundable by the usual method. For example, it is compoundable by the method of a description to JP,H10-45804,A.

[0034]As cellulose of the raw material of cellulose ester, although there is no limitation in particular, a kenaf besides cotton linters and wood pulp etc. can be mentioned. Mixed use of the cellulose ester obtained from them can be carried out at an arbitrary rate, respectively. Especially the cellulose ester obtained from cotton linters has the good detachability from a base material in the case of film production of a film, and it is preferred to it.

[0035]The number average molecular weight of the cellulose ester used for this invention has [the range of 70,000-300,000] a strongly preferred mechanical strength of a film. 80,000-200,000 are preferred.

[0036]As for the amount of free acid in the cellulose ester used for this invention, it is preferred in 1 kg of cellulose ester that it is 1.0 mol or less, and also its 0.3 mol or less is preferred to it, and especially its 0.1 mol or less is the most preferred to it. As for the amount of joint sulfuric acid in cellulose ester, 0.1g or less is preferred in 1 kg of cellulose ester as a sulfur atom, and also its 0.05g or less is preferred, and it is most preferred that it is especially 0.03g or less. The resistance to moist heat which was excellent in making the amount of free acid and the amount of joint sulfuric acid in cellulose ester into a mentioned range as a polarizing plate protective film or a base material for photographs can be given. The resistance to moist heat demanded as a polarizing plate protective film or a base material for photographs is a thing for which they are used and which degradation of decomposition, coloring, etc. does not produce as a severe

condition most even if placed, for example under 80 ° and 90%RH for 1,000 hours. The measuring method of the amount of free acid in cellulose ester and the amount of joint sulfuric acid can be measured by ASTM-D 817-96.

[0037]The cellulose ester film of this invention has the feature in at least one sort of compounds expressed with above-mentioned general formula (1) - (3) being included.

[0038]It is important for these compounds to excel in compatibility with cellulose ester and volatility-proof when it fabricates on a film.

[0039]The compound expressed with a general formula (1), for example An azelaic acid screw (2-ethylhexyl), Bis adipate (2-ethylhexyl), diisononyl adipate, Di-n-hexyl adipate, di-n-octyl adipate, di-n-decyl adipate, Diisodecyl adipate, diisobutyl adipate, dibutyl sebacate, A sebacic acid screw (2-ethylhexyl), screw dodecanedioate (2-ethylhexyl), \*\*\*\* is used preferably and an azelaic acid screw (2-ethylhexyl), bis adipate (2-ethylhexyl), a sebacic acid screw (2-ethylhexyl), and especially screw dodecanedioate (2-ethylhexyl) are especially preferred.

[0040]The compound expressed with a general formula (2) is trimellitic acid (2-ethylhexyl), for example.

[0041]The compounds expressed with a general formula (3) are trimethyl phosphate, phosphoric acid triethyl, tributyl phosphate, etc., for example.

[0042]The above-mentioned compound is a compound mainly known as a plasticizer for VCM/PVC or rubbers. It is a writer's making the cellulose ester solution which does not contain a chlorine-based solvent substantially contain these compounds, and manufacturing a film, and found out that the Rth value of a film could be reduced.

[0043]These compounds are marketed from two or more makers, and they can be preferably used for them. The above-mentioned compound may use two or more kinds together.

[0044]The content of the above-mentioned compound in a cellulose ester film has preferred 0.5 - 30 mass %, and it is still more preferred that it is two to 20 mass %. If there is too little content, the effect of Rth value reduction may not be acquired, and bleed out may be carried out if too large.

[0045]Although triphenyl phosphate and diethyl phthalate are conventionally known well as a plasticizer of cellulose ester, even if it makes these plasticizers contain, the effect of reducing a Rth value is not accepted.

[0046]The film production method of the cellulose ester film by the solution flow casting producing-film method concerning this invention is explained.

[0047]\*\* Melling process : it is the process of dissolving stirring this flake in a dissolution iron pot to the organic solvent which is mainly concerned with the good solvent to the flake of cellulose ester, and forming a dope.

[0048]How to perform under the pressure which a useful dissolving method is the temperature more than the boiling point of a main solvent, and is not boiled at this invention (it is called an

elevated-temperature solution process below). [ whether cellulose ester and an organic solvent are cooled at -100 °~-10 °, and ] Or after mixing cellulose ester with a -100 °~-10 ° organic solvent, the method (it is called a cooling solution process below) of warming at 0 °~-120 ° and the method (it is called a high voltage solution process below) of pressurizing cellulose ester and an organic solvent at 50 atmospheres - 2,000 atmospheres are mentioned. [0049]It is an elevated-temperature solution process, and when the case where methyl acetate (56.32 ° of boiling points) is used, for example as a main solvent is mentioned as an example, the temperature of 56.32 ° - 120 ° is preferred, and also is preferred. [ of 60 ° - 90 ° ] About 2 atmospheres or more of the pressure which is not boiled at this time may be sufficient, and although there is no maximum in particular, since an effect is saturated with about 50 atmospheres, 2-50 atmospheres is preferred. Further 2-10 atmospheres is preferred. [0050]The cellulose ester used for this invention has an acyl group of the carbon numbers 2-3 as a substituent. Although 2,6-3,0 are preferred for the degree of substitution of an acyl group, when the degree of substitution of an acyl group is 2.5 or more at this time, since using the above-mentioned cooling solution process and a high voltage solution process can acquire the good solubility to a non-chlorine solvent, it is desirable. [0051]About a cooling solution process, the method of forming a dope using solvents indicated in JP, H9-95538, A, 9-95544, and a 9-95557 gazette, such as acetone, methyl acetate, and ethyl formate, can be used. [0052]About a high voltage solution process, the high voltage dissolving method of a description can be used for JP, H11-21379, A. In a gazette, although acetone is used as an organic solvent, methyl acetate can be carried out similarly. [0053]As a useful non-chlorine organic solvent, by this invention, methyl acetate, ethyl acetate, Amyl acetate, acetone, a tetrahydrofuran, 1,3-dioxolane, 1,4-dioxane, cyclohexanone, ethyl formate, 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoro-1-propanol, 1,3-difluoro-2-propanol, 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol, 1,1,1,3,3,3-hexafluoro-2-propanol, 2,2,3,3,3-pentafluoro-1-propanol, nitroethane, etc. can be mentioned, and methyl acetate, ethyl acetate, and acetone can be used preferably. It is preferred that methyl acetate contains to all the organic solvents especially in more than 50 mass %. When acetone of 5 - 30 mass % is used together with methyl acetate to all the organic solvents, the viscosity of a dope can be reduced and it is desirable. [0054]If a chlorine-based solvent is not substantially included by this invention, it is most preferred that a chlorine-based solvent does not contain [ below 10 mass % ] at all in particular preferably to the total amount of organic solvents below in 5 mass %. [0055]It is preferred to make a cellulose ester dope contain alcohol with 1-4 carbon atoms of 0.1 - 30 mass % (as opposed to the total amount of organic solvents) other than the above-mentioned non-chlorine organic solvent. By thus, the thing for which alcohol which is a poor

solvent of cellulose ester is used together. The ratio of alcohol in a dope increases, a web (dope film) gels, and the effect that it becomes easy to make a web strong and to exfoliate from the base material for flow casting is acquired as the solvent evaporates, when a dope is cast into the base material for flow casting. As alcohol with 1-4 carbon atoms, methanol, ethanol, n-propanol, iso-propanol, n-butanol, sec-butanol, and tert-butanol can be mentioned. The stability of a dope and the boiling point are [ among these ] also comparatively low, drying property is also good, and since there is no toxicity, ethanol is the most preferred. [0056]The solids concentration of a dope usually has preferred 10 - 40 mass %, and, as for dope viscosity, it is preferred to be prepared by the range of 100-500 poise from the point of acquiring the smoothness of a good film. [0057]The dope prepared as mentioned above is filtered and defoamed with a filtering medium, and is sent to a next step with a pump. [0058]In a dope, a plasticizer, a mat agent, ultraviolet-rays \*\*\*\*\*, an antioxidant, a color, etc. may be added. [0059]In this invention, since the compound of general formula (1) - (3) also plays the role of a plasticizer, a plasticizer may not be added anew, but a plasticizer may be added for other purpose. [0060]For example, phosphoric ester other than alkyl phthalyl alkyl glycolate and a general formula (3), aromatic carboxylate, citrate, etc. are mentioned in order to improve the moisture permeability-proof of a film. [0061]As alkyl phthalyl alkyl glycolate, For example, methylphthalyl methyl glycolate, ethylphthalyl ethyl glycolate, Propylphthalyl propyl glycolate, butyl phthalyl butyl glycolate, Octylphthalyl octyl glycolate, methylphthalyl ethyl glycolate, Ethylphthalyl methyl glycolate, ethylphthalyl propyl glycolate, Propylphthalyl ethyl glycolate, methylphthalyl propyl glycolate, Methylphthalyl butyl glycolate, ethylphthalyl butyl glycolate, Butylphthalyl methyl glycolate, butylphthalyl ethyl glycolate, Propylphthalyl butyl glycolate, butylphthalyl propyl glycolate, methylphthalyl octyl glycolate, ethylphthalyl octyl glycolate, octylphthalyl methyl glycolate, octylphthalyl ethyl glycolate, etc. are mentioned. As phosphoric ester, triphenyl phosphate, tricresyl phosphate, phenyldiphenyl phosphate, etc. can be mentioned, for example. As aromatic carboxylic acid ester, for example as phthalic ester, such as phthalic ester and citrate, For example, dimethyl phthalate, diethyl phosphate, dioctyl phthalate, diethylnonyl phthalate, etc. can mention acetyl triethyl citrate and acetyl tributyl citrate as citrate. [0062]Methylphthalyl methyl glycolate, ethylphthalyl ethyl glycolate especially, Propylphthalyl propyl glycolate, butyl phthalyl butyl glycolate, and octylphthalyl octyl glycolate are preferred, and ethylphthalyl ethyl glycolate is used especially preferably. Two or more sorts may use these alkyl phthalyl alkyl glycolate, mixing. [0063]The quantity of the plasticizer used for this purpose has preferred 1 - 30 mass % to

cellulose ester, and its 2 - 13 mass % is especially preferred.

[0064]It may add with cellulose ester and a solvent in the case of preparation of a cellulose ester solution, and these compounds may be added the inside of solution preparation, and after preparation.

[0065]A color is added in order to improve the yellow of a film. As for a tint, what can be colored gray which is looked at by the usual base material for photographs is preferred. However, since there is no necessity for prevention of light brake lines as a polarizing plate protective film unlike the base material for photographs, there may be little content, its 1-100 ppm are preferred at the mass ratio to cellulose ester, and 2 ppm - 50 ppm are still more preferred. Since cellulose ester is presenting yellow a little, blue and a purple color are used preferably. It may be made to become gray, combining two or more colors suitably.

[0066]If it is hard to slide on a film, films may block and it may be inferior to handling nature. In this case, a silica dioxide, a titanium dioxide, an aluminum oxide, zirconium oxide, it is preferred to make mat agents, such as inorganic particles, such as calcium carbonate, kaolin, talc, a calcination calcium silicate, a hydration calcium silicate, aluminum silicate, a magnesium silicate, and calcium phosphate, and a crosslinked polymer, contain. Since a silica dioxide can make Hayes of a film small especially, it is desirable. As for combination of a mat agent, it is preferred that Hayes of a film blends so that a dynamic friction coefficient may become 0.5 or less 0.6% or less. 0.01-1.0 micrometer and content has [a mat agent used for this purpose / 0.005 - 0.3 mass %] preferred mean particle diameter to cellulose ester.

[0067]Opportunity of a liquid crystal display used outdoors has also increased, and it is that it is also important to give a function which cuts ultraviolet rays into a polarizing plate protective film. As for an ultraviolet ray absorbent used for this purpose, it is preferred that there is no absorption in a light range, and a benzotriazol system compound, a benzophenone series compound, a salicylic acid system compound, etc. are mentioned. For example, 2-(2-hydroxy-5-methylphenyl) benzotriazol, 2-(2'-hydroxy-3' and 5'-di-*t*-butylphenyl) benzotriazol, 2-(2'-hydroxy-3'-di-*t*-butyl-5-methylphenyl) benzotriazol, 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-*n*-octoxybenzophenone, 4-dodecyloxy 2-hydroxybenzophenone, They are 2,2 and 4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, phenyl salicylate, a methyl salicylate, etc.

[0068]The addition of an ultraviolet ray absorbent has the preferred range of 0.5 - 20 mass % to cellulose ester, and its range of 0.6 - 5 mass % is still more preferred.

[0069]The compound of a hindered phenol system is used preferably and they are 2,6-di-*t*-butyl-*p*-cresol and pentaerythritol tetrakis in order to improve the resistance to moist heat of a film. [3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate] Triethylene glycol screw [3-(3-*t*-butyl-5-methyl-4-hydroxyphenyl) propionate] 1,6-hexane \*\*\*\*\* [3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate] 2,4-bis-(*n*-octylthio)-6-(4-hydroxy-3,5-di-*t*-butylanilino)-1,3,5-

triazine, a 2,2-thio-diethylenescrew [3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate] Octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate, *N,N*-hexa methylenebis (3,5-di-*t*-butyl-4-hydroxy-hydronalium thinner MAMIDO), 1,3,5-trimethyl 2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl) benzene, tris-(3,5-di-*t*-butyl-4-hydroxybenzyl)-isocyanurate, etc. are mentioned. It is especially 2,6-di-*t*-butyl-*p*-cresol and pentaerythritol tetrakis. [3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate] Triethylene glycol screw [3-(3-*t*-butyl-5-methyl-4-hydroxyphenyl) propionate] is preferred. For example, a *N,N*-screw [3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionyl] Phosphorus system processing stabilizer, such as metal deactivator of hydrazine systems, such as hydrazine, and tris (2,4-di-*t*-butylphenyl) phosphite, may be used together. 1 ppm - 1.0% of the addition of these compounds is desirable to cellulose ester at a mass ratio, and its 10-1,000 ppm are still more preferred. In addition, thermostabilizers, such as a salt of alkaline-earth metals, such as calcium and magnesium, may be added.

[0070]A spray for preventing static electricity, fire retardant, lubricant, oils, etc. may be further added suitably besides the above.

\*\* Flow casting process : send a dope to an application-of-pressure die through a pressurization mold fixed-quantity gear pump, and it is the process of casting a dope from an application-of-pressure die on the base material for flow casting of the endless metal belt or the rotating metal drum transported infinitely (it may only be henceforth called a base material), in a flow casting position. The surface of the base material for flow casting is a mirror plane. Although how to cast others has a doctor blade method which adjusts thickness with a blade, or a method by the reverse roll coater adjusted with the roll to rotate reversely in the cast dope film, the application-of-pressure die which preparation of the slit width of a cap portion can be performed and is easy to make thickness uniform is preferred. Although there are a coat hanger die, a T die, etc. in an application-of-pressure die, all are used preferably. In order to gather film production speed, two or more application-of-pressure dies may be formed on the base material for flow casting, and doped quantity may be divided and stratified.

[0071]\*\* Solvent evaporation process : it is a process which heats a web (how to call the dope film after casting the dope on the base material for flow casting is adopted a web) on the base material for flow casting, and evaporates a solvent. In order to evaporate a solvent, there are a method of carrying out heat transfer with a liquid, the method of carrying out heat transfer from a rear surface by radiant heat, etc. from the rear face of the method of puffing a wind from the web side, and/or a base material, but the method of rear-face liquid heat transfer has well preferred drying efficiency. The method of combining them is also preferred.

[0072]\*\* A peeling process : it is the process of exfoliating a web in which a solvent evaporated on a base material in a peeling position. A web which exfoliated is sent to a next step. If the amount of residual solvents of a web in a time of exfoliating (following formula) is too large not much, it will be hard to exfoliate, or if it exfoliates after making it fully dry on a base material

conversely, a part of web will separate on the way.

[0073]The amount of residual solvents can be expressed with the following formula.

amount of residual solvents (mass %) = -- ((M-N)/N) x100 -- here, M is mass in an arbitrary time of a web, and mass when N dries M at 110 ° for 3 hours.

[0074]Methods (since it exfoliates while there are many amounts of residual solvents as possible, film production speed can be gathered) of gathering film production speed include the gel casting method (gel casting) a residual solvent can exfoliate in many. It adds a poor solvent to cellulose ester into a dope, and there are a method of gelling, a method of lowering and gelling temperature of a base material, etc. after a dope casting. There is also a method of adding metal salt into a dope. By making it gel on a base material and strengthening a film, exfoliation can be brought forward and film production speed can be gathered. When there are more amounts of residual solvents and it exfoliates, if a web is too soft, smoothness will be spoiled at the time of exfoliation, or it is easy to generate TSURE and a vertical stripe by exfoliation tension, and the amount of exfoliation residual solvents can be decided on balance of reasonable velocity and quality.

[0075]\*\* Drying stage : it is the process of drying a web using the tenter device which clips and conveys the both ends of a web with the dryer and/or clip which let a web pass by turns on the roll arranged alternately, and convey it on it. Although it is common to both sides of a web to puff a hot wind as for the means of desiccation, there is also a means to apply and heat microwave instead of a wind. Not much rapid desiccation tends to spoil the smoothness of the film of completion. It is good for a residual solvent to perform desiccation by an elevated temperature from a below 8 mass % grade. It lets the whole pass, and drying temperature is 40 ° - 250 °, and 70 ° - 180 ° are usually preferred. What is necessary is for drying temperature and the amount of drying winds to differ from drying time, and just to choose a drying condition suitably with the solvent to be used, according to the kind of use solvent, and combination.

[0076]In the drying stage after exfoliating from the base material side for flow casting, it is going to contract a web to a cross direction by evaporation of a solvent. Contraction becomes large, so that it dries rapidly by high temperature. It is desirable when drying controlling this contraction as much as possible makes smoothness of the done film good. The method (tenter system) of, for example, making a cross direction dry a dry whole process as shown in JP,562-46825,A, or some processes with a clip from this viewpoint, carrying out width maintenance of the width both ends of a web is preferred.

[0077]\*\* Coiling process : it is the process of rolling round a web as a film after the amount of residual solvents becomes below 2 mass %. A film with good dimensional stability can be obtained by making the amount of residual solvents below into 0.4 mass %. What is generally used should just be used for the rolling-up method, it has a constant calibrated wrench

method, the constant tension method, the taper tension method, the program tension controlling method of internal stress regularly, etc., and should just use them properly.

[0078]It is good for regulation of the thickness of a cellulose ester film to control dope concentration, the amount of liquid sending of a pump, the slit gap of the cap of a die, the extrusion pressure of a die, the speed of the base material for flow casting, etc. so that it may become desired thickness. It is preferred to make the programmed feedback information feed back to each above-mentioned equipment, and to adjust it, using a thickness detection means as a means which makes thickness uniform.

[0079]In the process to the desiccation from immediately after the flow casting which lets the solution flow casting producing-film method pass, although it is also good to make atmosphere in a dryer into air, it may carry out by inert gas atmospheres, such as nitrogen gas and carbon dioxide. However, as for the danger of the explosion limit of the evaporation solvent in a drying atmosphere, it is a matter of course that it must always be taken into consideration.

[0080]A cellulose ester film produced by making it above constitutes a polarizing plate from being stretched by both sides of light polarizer via adhesives, such as acrylic, if needed. About a kind of light polarizer, there is no limitation in particular and A polyvinyl alcohol system film, What iodine and dichromatic dye were made to stick to hydrophilic high polymer films, such as a partial formalized polyvinyl alcohol system film and an ethylene-vinyl acetate copolymer system partial saponification film, and was extended, Polyene oriented films, such as a dehydrating treatment thing of polyvinyl alcohol and a dechlorination thing of polyvinyl chloride, etc. are used. A polarizing plate using a cellulose ester film of this invention becomes able [ a polarization degree ] to consider it as a liquid crystal display which was excellent in a view angle characteristic according to making it cooperate with various liquid crystal cells, such as STN, TFT, TN, FCL, and SH, highly.

[0081]When using a cellulose ester film of this invention as a polarizing plate protective film, as for the film thickness, 20-200 micrometers is preferred, and its 30-90 micrometers are especially preferred. Below 500 g/m<sup>2</sup> and 24H preferably moisture vapor transmission of a film a dynamic friction coefficient of 300g/m<sup>2</sup> and 24H, and a film surface, Hayes of 0.5 or less and a film an elastic modulus of a film 0.6% or less, An absolute value (Re) of a retardation value to vertical incident light to 2.45 or more GPa and a film plane, As for an absolute value of a retardation value to incident light of an oblique direction of 45 degrees, it is [ an absolute value of a retardation value of 0-30 nm and a thickness direction ] preferred from 0-10 nm and a film plane that it is 0-70 nm. When such weighted solidity is the above-mentioned ranges shows the characteristic good as a polarizing plate protective film.

[0082]Moisture vapor transmission is measured under the conditions of 25 ° and 90%RH according to JIS Z2028-76.

[0083]Although an embodiment is given and this invention is explained in detail hereafter, the

mode of this invention is not limited to this.

[0084]

[Working example] Each measurement in an embodiment and a valuation method were performed by the following methods.

[0085] The <degree of substitution of cellulose ester> The degree of substitution shall be measured by the saponifying method. After weighing the dry cellulose reed rate precisely and dissolving in the mixed solvent (capacity factor 4:1) of acetone and dimethyl sulfoxide, predetermined 1N sodium hydroxide solution is added, and it saponifies at 25 ° for 2 hours. Phenolphthalein is added as an indicator and superfluous sodium hydroxide is titrated with 1N sulfuric acid. A blank test is done by the same method as the above. The supernatant liquid of the solution which titration furthermore ended is diluted, and the presentation of organic acid is measured with a conventional method using an ion chromatograph. And the degree of substitution (%) is computed according to the following.

[0086]

$$TA = (Q - P) \times F / (1000 \times W)$$

$$DS_{\text{Ac}} = (162.14 \times TA) / (142.14 \times TA + (1.56 \times TA) \times (AL/AC))$$

$$DS_{\text{Ac}} = S_{\text{Ac}} \times (AL/AC)$$

The amount of 1N sulfuric acid (ml) which titration of a sample takes among a formula to P, the amount of 1N sulfuric acid which a blank test takes to Q (ml), A mole ratio of acetic acid (AC) which TA measured potency of 1N sulfuric acid and W with sample mass (g), and measured it by all the organic acid contents (mol/g) and in which F measured AL/AC by an ion chromatograph, and other organic acid (AL), and DS<sub>Ac</sub> show the degree of substitution of an acetyl group, and DS<sub>Ac</sub> shows the degree of substitution of an acyl group of the amount 3 or 4 of carbon atoms.

[0087] <Number average molecular weight of cellulose ester> It measures by a following condition by high speed liquid chromatography.

[0088] solvent: -- methylene chloride column: -- MPWx1 (made by TOSOH CORP.)

sample concentration: -- 0.2 W/v% flow: -- a part for 1.0-ml/- sample injection-rate: --

300microl standard sample: -- polystyrene temperature: -- 23 ° <retardation value [ as opposed to vertical incident light to a film plane ] (Re value) and thickness direction retardation value (Rth value) > automatic double reflex meter KOBRA-21ADH. Using (a product made from Prince Measuring machine Machine), in 590 nm, wavelength performed three-dimensional refractometry and calculated the refractive index nx, ny, and nz under environment of 23 ° and 55%RH. According to a following formula, each retardation value (Re value, a Rth value) of a perpendicular direction and a thickness direction was computed.

[0089] Re value =  $(n_x - n_y) / (Rth \text{ value}) \times (2 - n_z) \times d$  (a refractive index of a film in a direction with nx parallel to the film production direction of a film.) A refractive index of a film in a

direction with ny vertical to the film production direction and nz express a refractive index of a film in a thickness direction, and d expresses thickness (nm) of a film, respectively.

A <polarization degree> Two polarizing plates were piled up and transmissivity in wavelength of 550 nm was measured using a spectrophotometer. At this time, Tp and transmissivity at the time of making it intersect perpendicularly mutually were set to Tc for transmissivity at the time of making a polarization axis of two polarizing plates parallel, and it asked for the polarization degree P with a following formula.

$$[0090] \text{Not less than } 99.0\% \text{ of } P \text{ is desirable from practically as } P(\%) = \{(Tp - Tc) / (Tp + Tc)\} \times 100 \text{ polarizing plate.}$$

[0091] Cellulose acetate (number average molecular weight 170,000) 100 mass part of the degree 2.88 of embodiment 1 acetylation, Tinuvin 326 (made by Ciba Specialty Chemicals) 0.5 mass part, Tinuvin 109 (made by Ciba Specialty Chemicals) 0.5 mass part, Tinuvin 171 (made by Ciba Specialty Chemicals) 0.5 mass part, Aerosil 200V (product made from Japanese Aerosil), ethylphthalyl ethyl glycolate 2 mass part, and trimethyl phosphate 10 mass part were mixed and swollen to a mixed solvent of methyl-acetate 450 mass part and acetone 50 mass part. Next, this mixture was put into a well-closed container of dual structure, and a refrigerant was introduced into an outside jacket, stirring a mixture slowly. This cooled a mixture in an inner container to -70 °. It cooled for 30 minutes until a mixture was cooled uniformly. A refrigerant in a jacket of the outside of a well-closed container is discharged, and warm water is instead introduced into a jacket. Then, contents were stirred and it raised to 100 ° over 40 minutes. Inside of a container became 2.5 atmospheres. Temperature was lowered to 50 °, and it returned to ordinary pressure, stirring, and was neglected as it is overnight, and a dope was obtained. This dope is filtered using Azumi filter paper No.244 made of Azumi Filter paper, fine one by Nippon Seisen Co., Ltd. -- it filtered by filtration pressure 0.98MPa using the helmet NM (absolutely filtering accuracy of 100 micrometers), and fine pore NF (it is absolutely used one by one in order (filtering accuracy of 50 micrometers, 15 micrometers, and 5 micrometers), raising filtering accuracy), and film production was presented.

[0092] The obtained dope was cast on the stainless steel belt from the die. After drying for 1 minute on the stainless steel belt by which contacted warm water with a temperature of 35 ° and temperature control was carried out from the rear face of the stainless steel belt, and also after contacting 15 ° chilled water at the rear face of the stainless steel belt and holding it for 15 seconds at it, it stripped off from the stainless steel belt. The amount of residual solvents in the film at the time of exfoliation was 40 mass %.

[0093] Subsequently, it was made to dry for 10 minutes at 130 °, fixing the both ends of the stripped-off film, and the film of 80 micrometers of thickness was obtained. The dipping of the obtained film was carried out to 80 ° and 2N sodium hydroxide solution for 2 minutes, it was rinsed, it dried for 10 minutes at 100 °, and the alkali treatment sample film was obtained. The



vertical retardation value (Re value) and thickness direction retardation value (Rt value) to incident light were measured to the film plane. The result was shown in Table 1.

[0094]Next, the 120-micrometer-thick polyvinyl alcohol film was immersed in solution 100 mass part containing iodine 1 mass part and boric acid 4 mass part, it extended 4 times at 50 °, and the polarization film was made. Completeness saponification type polyvinyl alcohol 5% solution was used for both sides of this polarization film as a binder, said alkali treatment sample film was pasted together to them, and the polarizing plate was produced. The polarization degree was measured using the obtained polarizing plate. The evaluation result was shown in Table 1.

[0095]Cellulose acetate (number average molecular weight 170,000) 100 mass part of the degree 2.88 of embodiment 2 acetylation, Tinuvin 326 (made by Ciba Specialty Chemicals) 0.5 mass part, Tinuvin 109 (made by Ciba Specialty Chemicals) 0.5 mass part, Tinuvin 171 (made by Ciba Specialty Chemicals) 0.5 mass part, Aerosil 200V (product made from Japanese Aerosil), ethylphthalyl ethyl glycolate 2 mass part, and trimethyl phosphate 10 mass part were mixed and swollen to a mixed solvent of methyl-acetate 450 mass part and acetone 50 mass part. Next, this mixture was fed into an application-of-pressure well-closed container, and a pressure of 1,000 atmospheres was applied for 30 minutes. A pressure was opened wide after that and it was considered as ordinary pressure. A repetition dope was obtained for this operation 3 times.

[0096]After filtering this dope using Azumi filter paper No.244 made of Azumi Filter paper, it settled overnight and deformed. subsequently, fine one by Nippon Seisen Co., Ltd. -- it filtered by filtration pressure 0.98MPa using the helmet NM (absolutely filtering accuracy of 100 micrometers), and fine pore NF (it is absolutely used one by one in order (filtering accuracy of 50 micrometers, 15 micrometers, and 5 micrometers), raising filtering accuracy), and film production was presented.

[0097]Using an obtained dope, like Embodiment 1, an 80-micrometer-thick film was produced and a polarizing plate sample was produced. An evaluation result was shown in Table 1.

[0098]In embodiment 3 Embodiment 1, except having replaced with trimethyl phosphate and having considered it as azelaic acid bis(2-ethylhexyl) 10 mass part, similarly, the 80-micrometer-thick cellulose ester film was produced, and the polarizing plate sample was produced. The evaluation result was shown in Table 1.

[0099]In embodiment 4 Embodiment 2, except having replaced with trimethyl phosphate and having considered it as azelaic acid bis(2-ethylhexyl) 10 mass part, similarly, the 80-micrometer-thick cellulose ester film was produced, and the polarizing plate sample was produced. The evaluation result was shown in Table 1.

[0100]In embodiment 5 Embodiment 1, except having replaced with trimethyl phosphate and having considered it as tris(trimellitic acid (2-ethylhexyl) 10 mass part, similarly, the 80-

micrometer-thick cellulose ester film was produced, and the polarizing plate sample was produced. The evaluation result was shown in Table 1.

[0101]In embodiment 6 Embodiment 2, except having replaced with trimethyl phosphate and having considered it as tris(trimellitic acid (2-ethylhexyl) 10 mass part, similarly, the 80-micrometer-thick cellulose ester film was produced, and the polarizing plate sample was produced. The evaluation result was shown in Table 1.

[0102]In comparative example 1 Embodiment 1, the raw material to be used Cellulose acetate (number average molecular weight 170,000) 100 mass part of the degree 2.85 of acetylation, 2-(2-hydroxy-3' and 5'-di-*t*-butylphenyl) benzotriazol 1 mass part, Except having considered it as triphenyl phosphate 10 mass part, diethyl phthalate 2 mass part, methyl-acetate 450 mass part, and ethanol 50 mass part, similarly, the 80-micrometer-thick cellulose ester film was produced, and also the polarizing plate sample was produced. The evaluation result was shown in Table 1.

[0103]The degree 2.00 of substitution of embodiment 7 acetyl group, the degree 0.80 of substitution of a propionyl group, cellulose ester 100 mass part of the number average molecular weight 100,000, Trimethyl phosphate 10 mass part, tinuvin 326 (made by Ciba Specialty Chemicals) 0.5 mass part, Tinuvin 109 (made by Ciba Specialty Chemicals) 0.5 mass part, Tinuvin 171 (made by Ciba Specialty Chemicals) 0.5 mass part, Aerosil 200V (product made from Japanese Aerosil), methyl-acetate 210 mass part, and ethanol 90 mass part were supplied to the application-of-pressure well-closed container, and it warmed at 80 °, and container-internal-pressure power having been 5 atmospheres, and agitating it, cellulose ester was dissolved thoroughly and the dope was obtained. After having lowered dope temperature to 50 °, settling overnight and filtering this dope using Azumi filter paper No.244 made of Azumi Filter paper, it settled overnight and deformed. subsequently, fine one by Nippon Seisen Co., Ltd. -- it filtered by filtration pressure 0.98MPa using the helmet NM (absolutely filtering accuracy of 100 micrometers), and fine pore NF (it is absolutely used one by one in order (the filtering accuracy of 50 micrometers, 15 micrometers, and 5 micrometers), raising filtering accuracy), and film production was presented.

[0104]Using the obtained dope, like Embodiment 1, the 80-micrometer-thick film was produced and the polarizing plate sample was produced. The evaluation result was shown in Table 1.

[0105]In embodiment 8 Embodiment 7, except having replaced with trimethyl phosphate and having changed into azelaic acid bis(2-ethylhexyl) 10 mass part, a film of 80 micrometers of thickness was produced like Embodiment 7, and a polarizing plate sample was produced. An evaluation result was shown in Table 1.

[0106]In embodiment 9 Embodiment 7, except having replaced with trimethyl phosphate and having changed into tris(trimellitic acid (2-ethylhexyl) 10 mass part, a film of 80 micrometers of thickness was produced like Embodiment 7, and a polarizing plate sample was produced. An

evaluation result was shown in Table 1.

[0107]In comparative example 2 Embodiment 7, except having replaced with trimethyl phosphate and having considered it as diethyl phthalate 15 mass part, methyl-acetate 450 mass part, and ethanol 50 mass part, similarly, an 80-micrometer-thick cellulose ester film was produced, and also a polarizing plate sample was produced. An evaluation result was shown in Table 1.

[0108]

[Table 1]

	厚度 μm	Rt 値 nm	偏光率 %	
実施例 1	80	25	4	99.3
実施例 2	80	20	2	99.6
実施例 3	80	35	5	99.4
実施例 4	80	30	3	99.5
実施例 5	80	55	3	99.1
実施例 6	80	50	5	99.2
実施例 7	80	5	0	99.8
実施例 8	80	22	0	99.6
実施例 9	80	20	0	99.5
比較例 1	80	80	15	96.5
比較例 2	80	100	10	96.8

[0109]According to Table 1, it turns out that thickness direction retardation of a cellulose ester film concerning this invention serves as the characteristic lower than what is depended on a conventional method shown in a comparative example, and it excels in a polarization degree when it is considered as a polarizing plate.

[0110]

[Effect of the Invention]The cellulose ester dope was able to be prepared by this invention, without using a chlorine-based solvent, and the manufacturing method which obtains the cellulose ester film in which the retardation value (Rt value) of the thickness direction was reduced was able to be provided.

[Translation done.]

## \*NOTICES\*

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## CLAIMS

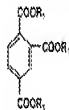
[Claim(s)]

[Claim 1] A cellulose ester film containing at least one sort of compounds expressed with a following general formula (1).

A general formula (1)  $R-OOC(CH_2)_n-COO-R$  [R expresses an alkyl group of the carbon numbers 1-10 among a formula, and n expresses an integer of 4-10.]

[Claim 2] A cellulose ester film containing at least one sort of compounds expressed with a following general formula (2).

[Chemical formula 1]  
→ 様式(2)



[R<sub>1</sub> expresses an alkyl group of the carbon numbers 1-8 among a formula.]

[Claim 3] A cellulose ester film containing at least one sort of compounds expressed with a following general formula (3).

[Chemical formula 2]  
→ 様式(3)



[R<sub>2</sub> expresses an alkyl group of the carbon numbers 1-4 among a formula.]

[Claim 4] A cellulose ester film of Claims 1-3, wherein cellulose ester is lower fatty acid ester of cellulose given in any 1 clause.

[Claim 5] A cellulose ester film of Claims 1-4, wherein cellulose ester has a number average molecular weight of 70,000-300,000 given in any 1 clause.

[Claim 6] To an organic solvent which does not contain a chlorine-based solvent substantially, at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (1) above the boiling point in ordinary pressure of the organic solvent, And a manufacturing method of a cellulose ester film exfoliating and drying a half-dry film which cast a dope produced by dissolving under pressure conditions on which it does not foam on a base material, and was cast into a base material.

[Claim 7] To an organic solvent which does not contain a chlorine-based solvent substantially, at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (2) above the boiling point in ordinary pressure of the organic solvent, And a manufacturing method of a cellulose ester film exfoliating and drying a half-dry film which cast a dope produced by dissolving under pressure conditions on which it does not foam on a base material, and was cast into a base material.

[Claim 8] To an organic solvent which does not contain a chlorine-based solvent substantially, at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (3) above the boiling point in ordinary pressure of the organic solvent, And a manufacturing method of a cellulose ester film exfoliating and drying a half-dry film which cast a dope produced by dissolving under pressure conditions on which it does not foam on a base material, and was cast into a base material.

[Claim 9] After cooling at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (1), and an organic solvent which does not contain a chlorine-based solvent substantially at -100 °~-10 °, A manufacturing method of a cellulose ester film exfoliating and drying a half-dry film which cast a dope which might be warmed by 0 °~-120 ° in the cooling thing on a base material, and was cast into a base material.

[Claim 10] A solution which might be pressurized by 50 atmospheres or more 2,000 atmospheres or less in a mixture of at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (1) and an organic solvent which does not contain a chlorine-based solvent substantially is cast on a base material. A manufacturing method of a cellulose ester film exfoliating and drying a half-dry film cast into a base material.

[Claim 11] After cooling at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (2), and an organic solvent which does not contain a chlorine-based solvent substantially at -100 °~-10 °, A manufacturing method of a cellulose ester film exfoliating and drying a half-dry film which cast a dope which might be warmed by 0

\*\* - 120 ° in the cooling thing on a base material, and was cast into a base material.

[Claim 12] A solution which might be pressurized by 50 atmospheres or more 2,000 atmospheres or less in a mixture of at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (2) and an organic solvent which does not contain a chlorine-based solvent substantially is cast on a base material, A manufacturing method of a cellulose ester film exfoliating and drying a half-dry film cast into a base material.

[Claim 13] After cooling at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (3), and an organic solvent which does not contain a chlorine-based solvent substantially at -100 ° to -10 °, A manufacturing method of a cellulose ester film exfoliating and drying a half-dry film which cast a dope which might be warmed by 0 ° to 120 ° in the cooling thing on a base material, and was cast into a base material.

[Claim 14] A solution which might be pressurized by 50 atmospheres or more 2,000 atmospheres or less in a mixture of at least one sort of a compound expressed with cellulose ester and the above-mentioned general formula (3) and an organic solvent which does not contain a chlorine-based solvent substantially is cast on a base material, A manufacturing method of a cellulose ester film exfoliating and drying a half-dry film cast into a base material.

[Claim 15] A manufacturing method of a cellulose ester film of Claims 6-14, wherein an organic solvent contains methyl acetate not less than 50% given in any 1 clause.

[Claim 16] A manufacturing method of a cellulose ester film of Claims 6-15, wherein cellulose ester is lower fatty acid ester of cellulose given in any 1 clause.

[Claim 17] A manufacturing method of a cellulose ester film of Claims 6-16, wherein cellulose ester has a number average molecular weight of 70,000-300,000 given in any 1 clause.

[Claim 18] A polarizing plate protective film using a cellulose ester film of Claims 1-5 given in any 1 clause.

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[Translation done.]